

## PATENT ABSTRACTS OF JAPAN

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(54) SURFACE TREATMENT METHOD FOR LONG MATERIAL AND OPTICAL FILM  
PRODUCED BY THE METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for depositing a uniform thin film on the surface of a long material by a discharge plasma treatment under the atmospheric pressure or near, and to provide an optical film produced thereby and various optical films for a display.

SOLUTION: A long material is arranged on the space between confronted electrodes. High frequency voltage is applied and discharged to the space between the electrodes while feeding reaction gas from a gas introduction part arranged in a slitlike way along the width direction of the long material provided on the space between the electrodes under the atmospheric pressure or near, so that a thin film is deposited on the surface of the base material.

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention about the long film formed by surface treatment method for forming a uniform thin film on a lengthy base material, and a method for the same, It is related with the optical film especially used for a solar cell, a liquid crystal image display device, various display devices, an organic electroluminescence display, an inorganic EL display, CRT, a plasma display, etc.

[0002]

[Description of the Prior Art]Improvement in transmissivity and contrast and the acid-resisting art of decreasing surface reflection for reflected reduction are conventionally proposed focusing on the field of the liquid crystal image display device etc. which are used for an optical lens, CRT, a computer, or a word processor. It is known that it is effective in acid-resisting art to decrease reflection of the light in a layered product and an air interface by adjusting the refractive index and optical film thickness of each class which are laminated as an optical interference layer to a suitable value. Such a multilayer layered product laminates  $\text{TiO}_2$ ,  $\text{ZrO}_2$ , and  $\text{Ta}_2\text{O}_5$  etc. as a high refractive index layer, and laminates  $\text{SiO}_2$ ,  $\text{MgF}_2$ , etc. as a low refractive index material, and it is manufactured.

These are manufactured by the dry type producing-film method for having used vacuums, such as sputtering process, a vacuum deposition method, and the ion plating method.

However, when the processed base material became large, since a film production device was enlarged dramatically, the device became very big-ticket, and also such vacuum devices spent time also on evacuation dramatically, and had the fault that productivity was not raised.

[0003]As a method of conquering the demerit of the underproductivity by using such vacuum devices, Plasma discharge is generated under an atmospheric pressure condition or the

pressure near the atmospheric pressure, and the method of producing a thin film is indicated to JP,11-133205,A, 11-61406, JP,2000-185362,A, 2000-147209, 2000-121804, etc.

[0004]However, even if it applied the method of the above-mentioned statement, the film production to very small area was possible, but the uniform film production to a wide substrate not less than 300 mm wide was difficult, and continuation film production of the acid-resisting functional membrane which needs to keep constant especially a refractive index and optical film thickness was dramatically difficult.

[0005]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the method of forming a uniform thin film on the surface of a lengthy base material, and the optical film manufactured by that cause by discharge plasma processing under atmospheric pressure or the pressure near the atmospheric pressure, and is providing the various optical films for displays.

[0006]

[Means for Solving the Problem]The purpose of describing this invention above was attained by the following means.

[0007]1., sending in reactant gas under atmospheric pressure or a pressure near the atmospheric pressure from a gas inlet which has been arranged inter-electrode [ which a lengthy base material counters ], and has been arranged at slit shape along with a width direction of a lengthy base material formed in inter-electrode. A surface treatment method of a lengthy base material making inter-electrode [ said ] impress and discharge high frequency voltage, and forming a thin film in a base material surface.

[0008]2., sending in reactant gas which has rare gas under atmospheric pressure or a pressure near the atmospheric pressure from a gas inlet arranged at slit shape along with a width direction of a lengthy base material formed in a counterelectrode which countered a lengthy base material and them which were wound around a rotating electrode and this about, and has been arranged. A surface treatment method of a lengthy base material making inter-electrode impress and discharge high frequency voltage, and forming a thin film in a base material surface.

[0009]3. Surface treatment method of lengthy base material given in said 1 providing two or more one electrodes of electrode which counters along transportation direction of substrate, and establishing said gas inlet or gas exhaust in electrode of inter-electrode [ of this plurality ], or this plurality itself.

[0010]4. Surface treatment method of lengthy base material given in said 2 providing two or more counterelectrodes countered and arranged to rotating electrode along transportation direction of substrate, and establishing said gas inlet or gas exhaust between counterelectrodes of this plurality, or in counterelectrode itself.

[0011]5. Surface treatment method of lengthy base material given in said 3, wherein said gas inlet and gas exhaust have been arranged by turns.

[0012]6. Surface treatment method of lengthy base material given in said 4, wherein said gas inlet and gas exhaust have been arranged by turns.

[0013]7. Surface treatment method of lengthy base material given in said 1 forming discharge restraint means near [ said ] gas inlet, or 2.

[0014]8. Surface treatment method of lengthy base material given in said 3 forming discharge restraint means near [ said ] gas inlet, or 5.

[0015]9. Surface treatment method of lengthy base material given in said 4 forming discharge restraint means near [ said ] gas inlet, or 6.

[0016]10. A surface treatment method of a lengthy base material given in said 4 and 6 carrying out suction immobilization, conveying a lengthy base material to a rotating electrode, and carrying out electrodischarge treatment to it, or 9.

[0017]11. A surface treatment method of a lengthy base material given in said 4, 6 and 9, wherein a rotating electrode is a conductive belt, or 10.

[0018]12. Gas of the same presentation is introduced from a gas inlet which has been arranged along the cross direction of a lengthy base material at slit shape and which were provided along a transportation direction, A surface treatment method of a lengthy base material given in said 3, 4, 5, 6, 8, 9 and 10, wherein a presentation of a layer forms an equal thin film in a thickness direction, or 11.

[0019]13. Two or more slit shape gas inlets are provided in accordance with the direction of a long picture along the cross direction of a lengthy base material, and gas of a presentation which is different from a gas inlet of this plurality is introduced, A surface treatment method of a lengthy base material given in said 3, 4, 5, 6, 8, 9 and 10, wherein a presentation of a layer forms a thin film which changes continuously or gradually in a thickness direction, or 11.

[0020]14. A surface treatment method of a lengthy base material given in said any 1 paragraph of 2-13, wherein reactant gas contains rare gas chosen from helium, argon, and neon 90 to 99.99% and contains an organic metallic compound 0.01 to 10%.

[0021]15. A surface treatment method of a lengthy base material given in said any 1 paragraph of 2-14, wherein frequency of high frequency voltage impressed to inter-electrode for discharge is 100 kHz - 150 MHz.

[0022]16. An optical film, wherein a surface treatment is carried out to said any 1 paragraph of 1-15 by a method of a statement.

[0023]17. A polarizing plate using an optical film of a statement for said 16 as a protective film.

[0024]18. A display using an optical film of a statement for said 16. Hereafter, this invention is explained in detail.

[0025]First, a surface treatment method which forms a thin film in the lengthy base material

surface of this invention is shown in drawing 1. Although a drawing is used for below and the embodiment is described to it about a manufacturing installation used for a method of manufacturing an optical film with a surface treatment method of this invention, and its manufacturing method, this invention is not limited to these. Drawing 1 is a schematic diagram showing an example of a plasma discharge processing unit used in a surface treatment method which forms a thin film in the lengthy base material surface of this invention. After the substrate F wound around rolled form was sent to the temperature-and-humidity controller 90 in drawing 1 and being conveyed by the carrying roll 11, Between the nip roll 12A formed in the spare room 60A introduced in rare gas, reactant gas, or its mixed gas and 12B is passed, accompanying air is intercepted, and it is led in the electrodischarge treatment device 70. Since it will become the hindrance of plasma treatment of the purpose if external air mixes in the electrodischarge treatment device 70, to prevent company of the open air as much as possible is desired. For that purpose, it is effective to provide many spare rooms or to increase the number of nip rolls.

[0026]In order to remove external air from the inside of the electrodischarge treatment device 70 and to introduce rare gas, reactant gas, or its mixed gas, the gas inlet 34 is established in the spare room 60A, the electrodischarge treatment device 70, and the spare room 60B mentioned later, respectively. The outlet 44 of gas is formed in the electrodischarge treatment device 70.

[0027]Thus, the substrate F led in the electrodischarge treatment device 70 is conveyed, touching the rotating electrode 25 with the guide roll 21. It can be rotated by the rotating electrode 25 synchronizing with conveyance of the substrate F. The substrate F is conveyed in the state where it stuck to the rotating electrode 25 to a discharge section. A discharge section is formed in a gap of the rotating electrode 25 and two or more counterelectrodes 24 which countered this and have been arranged. Between the rotating electrode 25 and two or more counterelectrodes 24, high frequency voltage is impressed via the voltage supply means 81 and 82 from the power supply 80. A gap of the rotating electrode 25 and the counterelectrode 24 is preferred in order to make discharge with stable it being usually 0.5-50 mm cause, and it is especially desirable that it is 1-20 mm. A gap of an electrode of the rotating electrode 25 and the counterelectrode 24 is preferred in order for a fixed thing to form a uniform thin film with a width direction. Two or more gas inlets 30a-30k (in drawing 1.) arranged to slit shape along with a width direction of a substrate between the front of a discharge section, and two or more counterelectrodes On substrate conveyance, the gas inlet 30a of the upstream is shown most, and it is omitted up to the gas inlet 30k most arranged to the downstream after 30b, Reactive gas is introduced towards a discharge section (formed in a gap of the rotating electrode 25 and two or more counterelectrodes 24 which countered this and have been arranged) from an arrow which shows a flow of gas having shown instead of a feed port being shown. As for

width of a slit of a gas inlet, 0.1-20 mm is preferred, and it is 1-10 mm more preferably. It is good to lean  $\pm 5-85$  degrees from a gas inlet, to a transportation direction preferably, although a gas introduction angle to the substrate F may be right-angled (it is shown that + inclines to an upstream direction of conveyance and - leans to a downstream direction).

[0028]An enlarged drawing of a discharge section by the side of the lowest style was shown in drawing 2. The gas inlets 30j and 30k showed signs that it was arranged between the counterelectrodes 24. After using reactant gas from a gas inlet through piping after generating in a reactant gas generation machine (not shown), having supplied a discharge section, it is discharged out of a device from the outlet 40 as exhaust gas.

[0029]Since dirt, such as an accumulated matter by reactive gas, adheres easily near the gas inlet of an electrode, it is preferred that a means by which discharge is controlled is formed. Although there is no restriction in particular as a means to control discharge, means which thicken solid dielectric thickness which manufactures a gas inlet with a non-metallic substance, for example or, with which only the portion covers an electrode, such as covering an electrode with an insulator and lengthening inter electrode distance slightly, are raised. It is not limited especially although fluoro-resins, such as Teflon (R), are preferably used as an insulator.

[0030]By reactant gas being supplied to a discharge section toward the substrate F stuck to the rotating electrode 25 from the counterelectrode 24 side from these gas inlets 30a-30k, and high frequency voltage being impressed between the rotating electrode 25 and the counterelectrode 24 which counters this. Plasma discharge starts in a discharge section between the counterelectrode 24 and the rotating electrode 25, supplied reactant gas becomes [ ionization or ] radical, and, thereby, a thin film is formed on a substrate.

[0031]Since electrodischarge treatment of the reactive gas introduced into discharge space is carried out for a short time, it is preferred that two or more gas inlets are provided along a transportation direction of the substrate F as mentioned above.

[0032]As for an interval which provides these gas inlets, it is preferred that it is 5-200 mm, and it is especially preferred that it is 10-100 mm. Introduced gas is sent to the substrate F and a gap of the counterelectrode 24 with conveyance of the substrate F. Gas used for processing may be discharged from gas exhaust (not shown) established in both ends of a width direction, and as shown in the front or drawing 1 of a discharge section, it may provide and discharge the gas exhaust 40 back.

[0033]Thus, the substrate F with which a thin film was formed by a discharge section passes along between the guide roll 22, the nip roll 12C of the spare room 60B, and 12D, is conveyed by the carrying roll 11, and is rolled round, or is sent to a next process. The divider plate 54 approaches said nip rolls 12A and 12B, and is arranged, and it controls that air accompanied to the substrate F advances into the plasma discharge processing unit 70. In order to prevent invasion of the open air, the nip rolls 12C and 12D formed in a spare room are approached,

and the divider plate 54 is formed similarly.

[0034]A schematic diagram showing an example of another plasma discharge processing unit concerning this invention is shown in drawing 3. Although the gas inlet 30a established in a method of the forefront of an electrodischarge treatment part, the gas exhaust 40a, and 40 f of gas exhaust established in a method of the last of an electrodischarge treatment part are shown like drawing 1 also in drawing 3, The gas inlets 30b-30f and the gas exhaust 40b-40f are formed by turns between counterelectrodes of plurality provided in the meantime which counter. In a figure, such gas inlets and gas exhaust which were established in a discharge section between the rotating electrode 25 and the counterelectrode 24 are omitted, and showed an arrow which only shows a flow of gas. Signs that a gas inlet and gas exhaust were established in inter-electrode by turns were shown using drawing 4 which is an enlarged drawing of a discharge section by the side of the lowest style.

[0035]Such gas inlets 30a-30f and gas exhaust 40a-40f are established in slit shape by each along the cross direction of a lengthy base material, By providing this by turns, it is supplied from each gas inlet and exhaust gas after being used for electrodischarge treatment in a discharge section between the rotating electrode 25 and the counterelectrode 24 has structure which can be discharged from gas exhaust which mainly adjoins. By this, more uniform processing is attained at a large discharge section, and the physical properties of a thickness direction of a thin film and a presentation which are formed can be made more into homogeneity. Or according to a transportation direction of the substrate F, it becomes it is also possible to change intentionally the physical properties of a thickness direction of a thin film or a presentation formed, and possible by changing concentration of reactant gas or a presentation, and an ingredient to make a thin film which has various functions by this form.

[0036]A gas inlet and gas exhaust do not need to be provided by turns strictly, and have just become the arrangement from which the above effects are acquired. A gas inlet and gas exhaust do not need to be arranged altogether each inter-electrode one, and one or more intervals are set and it may be arranged.

[0037]Furthermore drawing 5 is involved in this invention, it is an example of another plasma discharge processing unit, An example which established slit shape gas inlet 31 and gas exhaust 41 in counterelectrode 24 self by turns as a gas inlet provided between this, a rotating electrode, and a fixed electrode that counters besides the gas inlet 30 provided the front and behind an electrodischarge treatment part and the gas exhaust 40, and gas exhaust is shown. In order to supply gas to the slit shape gas inlet 31 cut by width direction uniformly, the buffer space 32 used as a buffer part is formed. Gas exhaust also has the same structure and, similarly is discharged via the buffer space 42.

[0038]A perspective view of the above-mentioned plasma discharge processing unit is shown in drawing 6. An arrow shows a flow of gas in the gas inlet 31 and the gas exhaust 41 which

were established in the gas exhausting pipe 43 which discharges gas through the gas introducing pipe 33 and the buffer space 42 which send reactant gas into the buffer space 32, and a counterelectrode along with a width direction of a substrate at slit shape, respectively. [0039]The electrode itself shows drawing 7 some examples of a counterelectrode which has reactant gas induction. (a) is the figure seen from the slanting front about a type which two or more gas inlets arranged all over a slot cut by electrode along with a width direction at the time of substrate conveyance at slit shape, respectively. (b) sees this from slanting back and a gas introducing pipe is omitted. (c) shows a sectional view which cut this perpendicularly along a feed port. (d) showed an example of that with which the gas inlet itself is cut by slit shape. It is desirable for a solid dielectric to be covered by these electrode surfaces (an inner surface is also included).

[0040]A gas inlet was leaned and established in (e) and (f) shows the section.

[0041]These counterelectrodes show drawing 8 an example of an electrodischarge treatment part of a plasma discharge processing unit provided with a gas supplying section.

[0042]In drawing 8, it is a thing using a counterelectrode of a type of (b) of said drawing 7, and an example which is later mentioned as a rotating electrode, for example, was combined with a belt electrode is shown. Reactant gas is introduced from the gas inlet 30 established in a counterelectrode, and gas used from the gas exhaust 40 established in the inter-electrode one for each sets discharges (an arrow showed a flow of reactant gas).

[0043]It is the circumference of a gas inlet or a decomposition product of reactant gas may be accumulated in a counterelectrode which has gas induction. Therefore, the gas induction circumference of an electrode around a gas inlet or an electrode thickens thickness of a solid dielectric which has covered an electrode so that discharge may be controlled, or covers it with an insulator, or its thing with a rotating electrode for which between is enlarged very much a little is preferably preferred. A thin film can be continuously formed on a lengthy base material by this for a long period of time.

[0044]In order to form a uniform thin film on a lengthy base material, where the substrate F is stuck on a rotating electrode, it is required to convey a discharge section. Therefore, a substrate is expected to be conveyed with suitable conveying tension so that a wrinkle etc. may not enter. It is also effective to carry out suction immobilization, to convey a substrate to a rotating electrode, and to carry out electrodischarge treatment to it, and it is preferred to carry out suction immobilization especially of the both ends in the width direction of a substrate.

[0045]In a method for forming thin film by a surface treatment method of a lengthy base material of this invention. It is more preferred than width of a lengthy base material that electrodischarge treatment is carried out on the long section and a rotating electrode in a transportation direction, therefore, as for a diameter of a rotating electrode, it is preferred that it is  $\frac{1}{3}$  or more [ of the \*\*\*\* length of a lengthy base material ], and it is desirable that they are



1 / two to 10 times.

[0046]An example of a plasma discharge processing unit which used a rotating electrode as a conductive belt is shown in drawing 9. When a rotating electrode is used as a conductive belt, since larger discharge space is securable, it is desirable. As for a belt, it is more effective than a rear face to suppress a deflection with a support roll etc., and it is preferred to make it inter-electrode spare time with a counterelectrode serve as approximately regulated. In drawing 9, 13A shows a conductive belt electrode, 14C and 14D are the support rolls of this conductive belt electrode, and 70 is an electrodischarge treatment device. A conductive belt electrode is countered, it has two or more counterelectrodes 24, and the gas inlet 30 and the gas exhaust 40 are established in each inter-electrode one by turns. Here, gas of an abbreviation same presentation can be introduced from the provided slit shape gas inlet 30, and a presentation of a layer of a thickness direction can form an equal thin film. I hope that it is not strictly the same in a presentation of gas being equal, for example, I hear that there may be about \*\*5% of change, and there is, I hear that that a presentation of a layer is also equal may differ in same grade, and there is, I hear that change of a grade which does not have a big difference chemically and physically is permitted, and there is.

[0047]A presentation or physical properties of a thin film in a thickness direction can also form a thin film which changes gradually or continuously by supplying gas of a presentation different, respectively from this provided slit shape gas inlet 30. A thin film which has various characteristics by this can be formed. Or in a layered product by which a multilayer thin film was laminated, adhesion with an adjacent layer is also improvable.

[0048]As for reactant gas used in order to form a thin film, it is preferred to contain rare gas preferably chosen from helium, argon, and neon 90.00 to 99.99%. Gas which contains an organic metallic compound, various organic compounds, or a fluorine-containing compound 0.01 to 10% is used here as a reactant ingredient.

[0049]As for high frequency voltage impressed to inter-electrode for plasma discharge processing, it is desirable that it is especially the frequency of 100 kHz - 150 MHz. A film in which frequency impressed for plasma discharge processing is formed at less than 100 kHz serves as porosity easily, a film becomes weak, and it is not desirable. It is difficult to obtain discharge space stable when 150 MHz was exceeded, and it is preferred that it is especially 50 MHz or less. This enables it to form a more uniform and firm film uniformly.

[0050]A schematic diagram showing an example of a cylindrical rotating electrode used for plasma discharge processing shown in drawing 1 for example, drawing 10 (a) and (b) starts this invention respectively, A schematic diagram showing an example of a cylindrical counterelectrode and drawing 12 (a) and (b) of drawing 11 (a) and (b) are the schematic diagrams showing an example of a square pillar type counterelectrode respectively.

[0051]In drawing 10 (a), the rotating electrode 25 comprises combination which covered the

lining processing dielectric 25b which provided an inorganic material in the conductive base materials 25a, such as metal, by lining. In drawing 10 (b), the rotating electrode 25 comprises combination of covering the ceramic coating processing dielectric 25B which carried out sealing of the ceramics after thermal spraying using an inorganic material to the conductive base materials 25A, such as metal. It comprises the combination same also about the counterelectrode 24 shown in drawing 11 (a) and (b), respectively, and the counterelectrode 24 shown in drawing 12 (a) and (b), respectively as the rotating electrode 25 shown in (a) of above-mentioned drawing 10, and (b).

[0052]Here, although metal, such as silver, platinum, stainless steel, aluminum, and iron, etc. are mentioned as the conductive base materials 25a and 25A, such as metal, and 24a and 24A, a viewpoint of processing to stainless steel is preferred. Although silicate system glass, borate system glass, phosphate system glass, germane acid chloride system glass, tellurite glass, aluminate glass, vanadate glass, etc. are preferably used as a lining material, Since it is easy to process borate system glass also in this, it is used still more preferably.

[0053]As a solid dielectric, in addition, plastics, such as polytetrafluoroethylene and polyethylene terephthalate, Multiple oxides, such as metallic oxides, such as glass, a silicon dioxide, an aluminum oxide ( $\text{aluminum}_2\text{O}_3$ ), zirconium oxide ( $\text{ZrO}_2$ ), and titanium oxide ( $\text{TiO}_2$ ), and barium titanate, etc. are mentioned.

[0054]In order that a counterelectrode or the rotating electrode can control temperature of a substrate, to have a temperature control function is desired. Although a temperature requirement to control changes with the purpose or a substrate to be used, it is desirable for there to be a function controllable to become temperature, such as 0 ° - 500 °, for example. a case where a weak substrate is used for heat -- especially -- room temperature - it is desirable for 200 ° to be further controllable in room temperature -120 ° in accuracy of less than ±1 °. A method of circulating a gas or a fluid by which temperature control was carried out in a rotating electrode as a temperature control method, etc. are preferred. As a fluid to be used, insulating materials, such as distilled water and an oil, are used preferably. In order to adjust to the above-mentioned temperature requirement, discharge plasma processing is carried out cooling an electrode and a substrate with an electrode refrigeration unit if needed.

[0055]When building these rotating electrodes and a counterelectrode (shown in drawing 10, 11, and 12 grades) into a plasma discharge processing unit which performs a surface treatment of this invention, an inter-electrode gap which counters is set, for example as about 1 mm.

[0056]The above-mentioned inter-electrode distance is determined in consideration of the purpose of using thickness of a solid dielectric, a size of impressed electromotive force, and plasma etc. As a distance of the solid dielectrics at the time of installing a solid dielectric in a

solid dielectric at the time of installing a solid dielectric in one side of the above-mentioned electrode, and the shortest distance of an electrode and both sides of the above-mentioned electrode, 0.5 mm - 20 mm are 1mm\*0.5mm desirable especially preferably from a viewpoint of generating discharge plasma uniform in any case.

[0057]The rotating electrode 25 and the counterelectrode 24 which counters this are arranged to a prescribed position in said plasma discharge processing unit 70, control of flow of the mixed gas generated with a reactant gas generating device is carried out, and mixed gas used for plasma treatment from the gas inlet 30 at a discharge section is supplied. Supplied gas is exhausted from the processing blasting-fumes outlet 40. Next, voltage is impressed to inter-electrode according to the power supply 80, the rotating electrode 25 is grounded to a ground, and discharge plasma is generated. Supply the substrate F via the carrying roll 11 here from a rolled form former volume substrate, and via the nip rolls 12A and 12B with the guide roll 21. Electrodischarge treatment of the surface is carried out by discharge plasma during conveyance, and the substrate F conveyed in a discharge section where one side contact (it is in contact with the rotating electrode 25) of inter-electrode is carried out is conveyed by next process via the nip rolls 12C and 12D via the guide roll 22 after that. Here, electrodischarge treatment is made only a field where the substrate F does not touch a rotating electrode.

[0058]Although a value of voltage impressed to the counterelectrode 24 from the power supply 80 is determined suitably, power supply frequency is adjusted to 1 kHz - 150 MHz. Although Pyrex (R) glass treatment containers etc. are preferably used for a plasma discharge processing unit, it is also possible to use metal if an insulation with an electrode can be taken. A metaphor may stick polyimide resin etc. on aluminum or an inner surface of a stainless frame, performs ceramic thermal spraying to this metallic frame, and is very good in insulation.

[0059]In this invention, although the above-mentioned discharge plasma processing is performed near atmospheric pressure or the atmospheric pressure, although a pressure of 20kPa - 200kPa is expressed, in order to acquire an effect of a statement preferably to this invention, 93kPa - 110kPa are preferred near the atmospheric pressure here.

[0060]In a plasma discharge processing unit concerning a surface treatment method of this invention, Being adjusted is preferred so that the maximum height ( $R_{max}$ ) of surface roughness specified by JIS B 0601 in an electrode of a side which touches a substrate in an electrode which counters mutually, especially a rotating electrode given in the above may be set to 10 micrometers or less, but. Preferably, the maximum of surface roughness is 8 micrometers or less, and it is adjusting to 7 micrometers or less preferably especially.

[0061]0.5 micrometer or less is desirable still more preferred, and center line average surface roughness ( $R_a$ ) specified by JIS B 0601 is 0.1 micrometer or less.

[0062]Next, mixed gas concerning a surface treatment method of this invention is explained. In order to form a thin film by this invention, mixed gas containing an organic metallic compound

or an organic matter is preferably used for rare gas. A thin film (layer) which has various functions, such as an optical interference layer (antireflection layer), a conductive layer, an antistatic layer, an infiltrative-proof layer, and a stain-proofing barrier, can be formed by changing reactant gas.

[0063]In order to produce a low reflection layered product with a surface treatment method of this invention (reflectance is made small), Mixed gas which it is preferred to adjust a refractive index, thickness, etc. of a thin film which are formed on a substrate to a desired value, and starts this invention from the viewpoint, What contained rare gas and organic gas containing organic metallic compounds, such as an organic fluorine compound, a silicon compound or a titanium compound especially organic silicon, or a titanium compound, at least is used. Here, mixed gas may contain compounds other than said statement as other ingredients.

[0064]As thickness of an obtaining-by above-mentioned surface treatment method thin film, a thin film of the range of 1 nm - 1000 nm is obtained.

[0065]With rare gas of the above-mentioned statement, although helium, neon, argon, krypton, a xenon, radon, etc. are mentioned the 18th group element, in order [ of the periodic table ] to specifically acquire an effect of a statement to this invention, helium, argon, and neon are used preferably.

[0066]As an organic fluorine compound of the above-mentioned statement, carbon fluoride gas, fluoridation hydrocarbon gas, etc. are used preferably. For example, 6 4 fluoridation [ methane ] ( $\text{CF}_4$ ), ethane fluoridation ( $\text{C}_2\text{F}_6$ ), 6 ethylene tetrafluoride ( $\text{CF}_2\text{CF}_2$ ), propylene fluoridation ( $\text{CF}_3\text{CFCF}_2$ ). Carbon fluoride compounds, such as 8 cyclobutane fluoridation ( $\text{C}_4\text{F}_8$ ); 2 methane fluoridation ( $\text{CH}_2\text{F}_2$ ). 4 4 fluoridation [ ethane ] ( $\text{CFH}_2\text{CF}_3$ ), propylene fluoridation ( $\text{CF}_3\text{CH}_2\text{CH}_2\text{F}$ ). Fluoridation hydrocarbon compounds, such as 3 propylene fluoridation ( $\text{CH}_2\text{CHCF}_3$ ), 12 fluoridation [ 13 fluoridation / methane / chloride ( $\text{CClF}_3$ ) and methane ] chloride ( $\text{CHClF}_2$ ). A fluoride substitution product of organic compounds, such as a halogenide of fluoridation hydrocarbon compounds, such as 24 fluoridation [ cyclobutane ] chloride ( $\text{C}_4\text{H}_2\text{Cl}_2\text{F}_4$ ), alcohol, acid, and ketone, is mentioned. These may be independent, or it may mix and they may be used.

[0067]As fluoridation hydrocarbon gas of the above-mentioned statement, 3 4 fluoridation [ 4 fluoridation / 2 fluoridation / methane / and ethane / and propylene ], propylene, fluoridation is mentioned.

[0068]Although a fluoride substitution product of organic compounds, such as a halogenide of fluoridation hydrocarbon compounds, such as 24 fluoridation [ 12 fluoridation / 13 fluoridation / methane / chloride and methane / chloride, cyclobutane, ] chloride, alcohol, acid, and ketone, can be used, it is not limited to these. These compounds may have an ethylene nature

unsaturation group in intramolecular.

[0069]The above-mentioned compound may be independent, or it may mix and it may be used. When using an organic fluorine compound of the above-mentioned statement into mixed gas, although it is preferred that it is 0.01 to 10 volume % as for content of an organic fluorine compound in [ a viewpoint of forming a uniform thin film on a substrate by discharge plasma processing to ] mixed gas, it is 0.1 to 5 volume % still more preferably.

[0070]When an organic fluorine compound is a gas in ordinary temperature and ordinary pressure, since it can be used as it is, a method of this invention can be most easily carried out as a constituent of mixed gas. However, when an organic fluorine compound is a fluid or a solid in ordinary temperature and ordinary pressure, what is necessary is just to use it, making it evaporate or sublime by methods, such as heating and decompression, and it may dissolve and use for a suitable solvent.

[0071]As a silicon compound of the above-mentioned statement, for example Organic metallic compounds, such as dimethylsilane and a tetramethylsilane, Metal halogenated compounds, such as metal hydride, such as a mono silane and a disilane, dichlorosilane, and trichlorosilane, Organosilicon compounds, such as alkoxysilane, such as a tetramethoxy silane, a tetraethoxysilane, dimethyl diethoxysilane, and tetra isopropoxysilane, and an organosilane, are raised, and although it is preferred to use especially an organosilicon compound, it is not limited to these. These can be combined suitably and can be used.

[0072]When using a silicon compound of the above-mentioned statement into mixed gas, although it is preferred that it is 0.1 to 10 volume % as for content of a silicon compound in [ a viewpoint of forming a uniform thin film on a substrate by discharge plasma processing to ] mixed gas, it is 0.1 to 5 volume % still more preferably.

[0073]When using a titanium compound as an organic metallic compound of the above-mentioned statement, Metal hydride, such as organic metallic compounds, such as tetra dimethylamino titanium, monotitanium, and JICHITAN, Although it is preferred to use organic titanium compounds, such as metal alkoxides, such as metal halogenated compounds, such as a titanium dichloride, titanium trichloride, and titanium tetrachloride, tetraethoxytitanium, tetraisopropoxy titanium, and tetrabutoxytitanium, it is not limited to these.

[0074]When using a titanium compound of the above-mentioned statement into mixed gas, although it is preferred that it is 0.1 to 10 volume % as for content of a titanium compound in [ a viewpoint of forming a uniform thin film on a substrate by discharge plasma processing to ] mixed gas, it is 0.1 to 5 volume % still more preferably.

[0075]As organic metallic compounds, such as a silicon compound of the above-mentioned statement, and a titanium compound, organic metallic compounds, such as a viewpoint on handling to a metal alkoxide, are preferred, there is no generating of corrosiveness and harmful gas, and dirt on a process, etc. are preferably used from few things.

coat layer and an antistatic layer can be used as a substrate.

[0082]As the above-mentioned base material (used also as a substrate), Specifically Polyester film, such as polyethylene terephthalate and polyethylenenaphthalate, A polyethylene film, a polypropylene film, cellophane, a cellulose-diacetate film, A cellulose-acetate-butylate film, a cellulose-acetate-propionate film, A cellulose acetate phthalate film, cellulose triacetate, A film which consists of cellulose ester or those derivatives, such as nitrocellulose, A polyvinylidene chloride film, a polyvinyl alcohol film, an ethylene vinyl alcohol film, A syndiotactic polystyrene system film, a polycarbonate film, A norbornene resin system film, a polymethylpentene film, a polyether ketone film, A polyimide film, a polyether sulfon film, a polysulfone system film, A polyether ketoneimide film, a polyamide film, a fluoro resin film, a nylon film, a polymethylmethacrylate film, an acrylic film, or a polyarylate system film can be mentioned.

[0083]these raw materials are independent – it is – it can also be used, being mixed suitably. Commercial items, such as ZEONEX (made by Nippon Zeon Co., Ltd.) and ARTON (made by Japan Synthetic Rubber Co., Ltd.), can be used especially. Even if it is a raw material with large peculiar double refraction factors, such as polycarbonate, polyarylate, polysulfone, and polyether sulphone, it can obtain by setting extension conditions etc. as conditions, such as solution flow casting and melting extrusion, and also length, and a transverse direction suitably. A base material concerning this invention is not limited to the above-mentioned statement. As thickness, a film (10 micrometers - 1000 micrometers) is used preferably.

[0084]Since a layered product that whose a cellulose ester film is used especially it is low reflectance as a base material concerning this invention is obtained, it is used preferably. From a viewpoint acquired preferably, an effect of a statement as cellulose ester to this invention Cellulose acetate, Cellulose acetate butylate and cellulose acetate propionate are preferred, and cellulose acetate butylate and cellulose acetate propionate are used preferably especially. As a butyryl group which forms butyrate, it may branch also by straight chain shape.

[0085]Cellulose acetate propionate which contains a propionate group as a substituent is excellent in a water resisting property, and useful as a film for liquid crystal image display devices.

[0086]When using cellulose ester as a substrate concerning this invention, there is no limitation in particular as cellulose of a raw material of cellulose ester, but cotton linters, wood pulp (the needle-leaf tree origin, broad-leaved tree origin), a kenaf, etc. can be mentioned. Mixed use of the cellulose ester obtained from them can be carried out at an arbitrary rate, respectively. These cellulose ester can obtain it using organic solvents, such as organic acid like acetic acid, and methylene chloride, by the ability to make a cellulose raw material able to react using a protonic catalyst like sulfuric acid, when an acylating agent is an acid anhydride (an acetic anhydride, a propionic anhydride, a butyric anhydride).

[0093]As shown in the following film production process, when drying a solvent from a web (dope film) formed on a base material in a solvent evaporation process, From a viewpoint which prevents foaming in a web, as the boiling point of an organic solvent used, 30-80 °C is preferred, for example, the boiling points of a good solvent of the above-mentioned statement are methylene chloride (40.4 °C of boiling points), methyl acetate (56.32 °C of boiling points), acetone (56.3 °C), ethyl acetate (76.82 °C), etc.

[0094]It is preferred that methylene chloride which is excellent in solubility, and methyl acetate are used preferably, and methylene chloride is especially contained to all the organic solvents also in a good solvent of the above-mentioned statement as for more than 50 mass %.

[0095]It is preferred to make alcohol with 1-4 carbon atoms of 0.1 - 30 mass % other than the above-mentioned organic solvent contain. It is preferred that said alcohol is especially contained by 10 - 30 mass % preferably. After casting a dope of the above-mentioned statement into a base material for flow casting, if a solvent begins evaporation and a ratio of alcohol increases, a web (dope film) will gel these, It is used as a gelling solvent which makes it easy to make a web strong and to exfoliate from a base material for flow casting, or there is also a role which promotes the dissolution of cellulose ester of a non-chlorine organic solvent when a rate has little these.

[0096]As alcohol with 1-4 carbon atoms, methanol, ethanol, n-propanol, iso-propanol, n-butanol, sec-butanol, tert-butanol, etc. can be mentioned.

[0097]The stability of a dope and the boiling point are [ among these ] also comparatively low, drying property is also good, and since there is no toxicity, ethanol is preferred. It is preferred to use a solvent which contains the ethanol 10 - 30 mass % to the methylene chloride 70 - 90 mass % preferably. Methyl acetate can also be used instead of methylene chloride as a good solvent. In this case, a cellulose ester solution can be prepared using a cooling solution process which cools and dissolves in -100 °C--10 °C.

[0098]When using a cellulose ester film for a base film in a surface treatment method of this invention, it is preferred to contain a plasticizer in this cellulose ester film.

[0099]Although there is no limitation in particular as a plasticizer, a phosphoric ester system plasticizer, a phthalate ester plasticizer, a trimellitic acid ester system plasticizer, a pyromellitic acid system plasticizer, a glycolate system plasticizer, a citrate plasticizer, etc. can be used preferably. In a phosphoric ester system, triphenyl phosphate, tricresyl phosphate, Cresyl diphenyl phosphate, octyl diphenyl phosphate, By a phthalic ester system, diphenylbiphenyl phosphate, trioctylphosphate, tributyl phosphate, etc. Diethyl phthalate, dimethoxyethyl phthalate, dimethyl phthalate, dioctyl phthalate, dibutyl phthalate, di-2-ethylhexyl phthalate, butylbenzyl phthalate, etc. as a trimellitic acid system plasticizer, Tributyl trimellitate, triphenyl trimellitate, triethyl trimellitate, etc. as a pyromellitic acid ester system plasticizer, By a glycolic-acid-ester system, tetrabutyl pyromellitate, tetraphenyl pyromellitate, tetraethyl pyromellitate,



etc. A triacetin, tributyrin, ethylphthalyl ethyl glycolate, methylphthalyl ethyl glycolate, butyl phthalyl butyl glycolate, etc. as a citrate plasticizer, Triethyl citrate, tri-n-butyl citrate, acetyl triethyl citrate, acetyltri-n-butyl citrate, Acetyltri-n-(2-ethylhexyl) citrate etc. can be used preferably.

[0100]It is preferred independent or to use these plasticizers together. The amount of these plasticizers used is points, such as film performance and processability, and it is preferred that it is one to 20 mass % to cellulose ester.

[0101]An ultraviolet ray absorbent concerning a base material used by this invention is explained. As an optical film of this invention, an ultraviolet ray absorbent is preferably used from a viewpoint of deterioration prevention, such as a liquid crystal.

[0102]As an ultraviolet ray absorbent, it excels in absorption power of ultraviolet rays with a wavelength of 370 nm or less, and what has the few visible absorption of light with a wavelength of not less than 400 nm is preferably used from a viewpoint of good liquid-crystal-display nature. As an example of an ultraviolet ray absorbent preferably used for this invention, although a oxy benzophenone series compound, a benzotriazol system compound, a salicylate system compound, a benzophenone series compound, a cyanoacrylate system compound, a nickel complex salt system compound, etc. are mentioned, for example, It is not limited to these.

[0103]Although an example of an ultraviolet ray absorbent concerning this invention is given to below, this invention is not limited to these.

[0104]UV-1:2-. (2'-hydroxy-5'-methylphenyl) benzotriazol UV-2:2- (2'-hydroxy-3'.) 5'-di-tert-buthylphenyl benzotriazol UV-3:2-(2'-hydroxy-3'-tert-butyl-5'-methylphenyl) benzotriazol UV-4:2- (2'-hydroxy-3'.) 5'-di-tert-buthylphenyl-5-chlorobenzotriazole UV-5:2-(2'-hydroxy-3'-(3"-, 4"-, 5"6"-tetrahydro phthalimidomethyl)-5'-methylphenyl) benzotriazol UV-6 : 2,2-methylene bis. (4-(1,1,3,3-tetramethylbutyl)-6-(2H-benzotriazol 2-yl) phenol)

UV-7:2-. (2'-hydroxy-3'-tert-butyl-5'-methylphenyl)-5-chlorobenzotriazole UV-8:2-(2H-benzotriazol 2-yl)-6-(straight chain and side chain dodecyl)-4-methyl phenol (TINUVIN171, product made from Ciba)

UV-9: Octyl- 3 - [3-tert-butyl-4-hydroxy-5-(chloro-2H-benzotriazol 2-yl) phenyl] Propionate and 2-ethylhexyl 3 - [3-tert-butyl-4-hydroxy-5-(5-chloro-2H-benzotriazol 2-yl) phenyl] A mixture of propionate (TINUVIN109, product made from Ciba)

Although an example of a benzophenone series compound is shown below, this invention is not limited to these.

[0105]UV-10 :. 2,4-dihydroxybenzophenone UV-11:2,2'-dihydroxy-4-methoxybenzophenone UV-12:2-hydroxy-4-methoxy-5-sulfobenzophenone UV-13: Screw (2-methoxy-4-hydroxy-5-benzoyl phenylmethane)

An ultraviolet ray absorbent of the above-mentioned statement preferably used by this



invention, A benzotriazol system ultraviolet ray absorbent whose benzotriazol system ultraviolet ray absorbent and benzophenone series ultraviolet ray absorbent excellent in an effect which prevents degradation of a polarizing plate and a liquid crystal transparency is high and are preferred and which has less unnecessary coloring is used especially preferably.

[0106]As for retardation  $R_0$  within a field, as an optical property of a substrate concerning this invention, a 0-1000-nm thing is used preferably, and, as for thick ally-oriented retardation  $R_t$ , a 0-300-nm thing is preferably used according to a use.

[0107]The surface treatment method of this invention can also form a thin film by a method of this invention on a coating layer provided on a substrate, although it is also possible to form a thin film directly on the surface of a substrate. An antistatic layer, a conductive layer, a hard coat layer, an anti-glare layer, an optical interference layer, refractive index layers, a back coat layer, etc. which a limit in particular does not have about a kind of coating layer, for example, were provided by spreading are raised. In order to form a thin film on a resin layer which an ingredient containing an ethylene nature unsaturated monomer was polymerized, and was formed even especially in inside, it can use preferably.

[0108]Although a layer which contains actinic-rays hardening resin or heat-curing resin as a constituent is preferably used as a resin layer which an ingredient containing an ethylene nature unsaturated monomer was polymerized, and was formed, especially being used preferably is an actinic-rays cured resin layer.

[0109]Here, an actinic-rays cured resin layer means a layer which uses as a main ingredient resin hardened through crosslinking reaction etc. by actinic-rays exposure like ultraviolet rays or an electron beam. Although ultraviolet curing nature resin, electron beam hardening resin, etc. are mentioned as a typical thing as actinic-rays hardening resin, resin hardened by the actinic-rays exposure of those other than ultraviolet rays or an electron beam may be sufficient. As ultraviolet curing nature resin, for example Ultraviolet curing type acrylic urethane system resin, Ultraviolet curing type polyester-acrylates system resin, ultraviolet curing type epoxy acrylate system resin, ultraviolet curing type polyol acrylate system resin, or an ultraviolet curing type epoxy resin can be mentioned.

[0110]Generally ultraviolet curing type acrylic urethane system resin to polyester polyol An isocyanate monomer, To output acquired by making a prepolymer react, further Or 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate (only acrylate is displayed on acrylate below as what includes methacrylate), It can obtain easily by making a monomer of an acrylate system which has hydroxyl groups, such as 2-hydroxypropyl acrylate, react (see JP,59-151110,A etc.).

[0111]Ultraviolet curing type polyester-acrylates system resin can be easily obtained by making a monomer of 2-hydroxyethyl acrylate and a 2-hydroxy acrylate system react to

polyester polyol generally (see JP,59-151112,A).

[0112]As an example of ultraviolet curing type epoxy acrylate system resin, epoxy acrylate can be made into oligomer and a thing which made reactive diluent and a photoreaction initiator add and react to this can be mentioned (for example, JP,1-105738,A). As this photoreaction initiator, it can be used from inside of a benzoin derivative, an oxime ketone derivative, a benzophenone derivative, a thioxan ton derivative, etc., being able to choose one sort or two sorts or more.

[0113]As an example of ultraviolet curing type polyol acrylate system resin, Trimethylolpropane triacrylate, ditrimethylolpropanetetraacrylate, pentaerythritol -- doria -- KURIRETO, pentaerythritol tetraacrylate, dipentaerythritol hexaacrylate, alkyl modification dipentaerythritol pentaacrylate, etc. can be mentioned.

[0114]These resin is usually used with a publicly known photosensitizer. The above-mentioned photoreaction initiator can also be used also as a photosensitizer. Specifically, these derivatives, such as an acetophenone, benzophenone, hydroxybenzophenone, MIHIRAZU ketone, alpha-amylomaize Qeshm ester, and a thioxan ton, can be mentioned. Sensitizers, such as n-butylamine, triethylamine, and tri-n-butyl phosphine, can be used in the case of use of a photoreaction agent of an epoxy acrylate system. As for a photoreaction initiator and a photosensitizer which are contained in an ultraviolet curing nature resin composition except a solvent component which volatilizes after spreading desiccation, it is preferred that it is 2.5 to 6 mass [ of this constituent ] %.

[0115]As a resin monomer, an unsaturated double bond can mention general monomers, such as methyl acrylate, ethyl acrylate, butyl acrylate, vinyl acetate, benzyl acrylate, cyclohexyl acrylate, and styrene, as one monomer, for example. Make two or more unsaturated double bonds into a monomer which it has, and Ethylene glycol diacrylate, Propylene glycol diacrylate, divinylbenzene, 1,4-cyclohexane diacrylate, 1,4-cyclohexyldimethyl horse mackerel acrylate, the above-mentioned trimethylolpropane triacrylate, pentaerythritol tetra acrylic ester, etc. can be mentioned.

[0116]as ultraviolet curing resin -- ADEKAOPUTOMA KR-BY series:KR-400 and KR-410, KR-550, KR-566, KR-567, and BY-320B (above) Asahi Denka Kogyo K.K. make or KOEI hard A-101-KK, A-101-WS, C-302, C-401-N, C-501, M-101, M-102, T-102, D-102, NS-101, FT-102Q8, MAG-1-P20, and AG-106 and M-101-C (above) The Koei Chemical, Inc. make or the Seika beam PHC2210 (S), PHC X-9 (K-3), PHC2213, DP-10, DP-20, DP-30, P1000, P1100, P1200, P1300, P1400, P1500, P1600, SCR900 (above) The Dainichiseika Colour & Chemicals Mfg. Co., Ltd. make or KRM7033, KRM7039, KRM7130, KRM7131, UVECRYL29201, UVECRYL29202 (above) Die cell you CB, Inc. or RC-5015, RC-5016, RC-5020, RC-5031, RC-5100, RC-5102, RC-5120, RC-5122, RC-5152, RC-5171, RC-5180, RC-5181 (above) the Dainippon Ink & Chemicals, Inc. make or OREKKUSUNo.340 -- clear (made by Chugoku

Marine Paints, Ltd.). Or Sun Ladd H-601 (made by Sanyo Chemical Industries, Ltd.) or SP-1509, SP-1507 (made by Showa High Polymer Co., Ltd.), Or it chooses from a thing of RCC-15C (made by Grace Japan, Inc.), ARONIKKUSU M-6100, M-8030, M-8060 (above, Toagosei, Inc. make), or other marketing suitably, and can use.

[0117]An actinic-rays cured resin layer used for this invention can be painted by a publicly known method. Either can be used if it is a light source which generates ultraviolet rays as a light source for forming a cured film layer for actinic-rays hardening resin by a photo-curing reaction. For example, a low pressure mercury lamp, a medium-voltage mercury-vapor lamp, a high-pressure mercury-vapor lamp, an ultrahigh pressure mercury lamp, a carbon arc lamp, a metal halide lamp, a xenon lamp, etc. can be used. Although exposure conditions change with each lamps, there should just be irradiation light quantity of a  $20\text{--}10000\text{ mJ/cm}^2$  grade, and is  $50\text{--}2000\text{ mJ/cm}^2$  preferably. It can be used by using a sensitizer which is missing from a near ultraviolet ray field - a visible ray region, and has absorption maximum in the field.

[0118]A solvent which paints a resin layer which contains an above-mentioned back coat layer and a conductive particle as a solvent at the time of painting an actinic-rays cured resin layer, For example, it chooses suitably from solvents of hydrocarbon, alcohols, ketone, ester species, glycol ether, and others, or these can be mixed and used. Preferably, a solvent which contains [ more than 5 mass % ] still more preferably propylene glycol mono- (alkyl group of carbon numbers 1-4) alkyl ether or propylene glycol mono- (alkyl group of carbon numbers 1-4) alkyl ether ester in more than 5 - 80 mass % is used.

[0119]As a coating method of ultraviolet curing nature resin composition coating liquid, publicly known methods, such as a photogravure coating machine, a spinner coating machine, a wire bar coating machine, a roll coater, a reverse coating machine, an extrusion coating machine, and an air doctor coating machine, can be used. In wet thickness, 0.1-30 micrometers is suitable for coverage, and it is 0.5-15 micrometers preferably. Spreading speed is performed by a part for 10-100-m/.

[0120]An ultraviolet curing nature resin composition irradiates with ultraviolet rays from a light source, after spreading desiccation is carried out, but 0.5 second - 5 minutes of irradiation time are good, and it is more preferred from hardening efficiency of ultraviolet curing nature resin, and working efficiency. [ of 3 seconds - 2 minutes ]

[0121]In this way, it is preferred to add inorganic or organic particles to an obtained cured film layer, in order to prevent blocking, and in order to improve opposite abrasion nature etc. As inorganic particles, for example, silicon oxide, titanium oxide, an aluminum oxide, Can mention tin oxide, a zinc oxide, calcium carbonate, barium sulfate, talc, kaolin, calcium sulfate, etc., and as organic particulates, Polymethacrylic acid methyl acrylate resin powder, acrylic styrene resin powder, Polymethyl-methacrylate-resin powder, silicon system resin powder,

polystyrene-system-resin powder, Polycarbonate resin powder, benzoguanamine system resin powder, melamine system resin powder, Polyolefin-system-resin powder, polyester system resin powder, polyamide system resin powder, polyimide system resin powder, or polyfluoroethylene system resin powder can be mentioned, and it can add to an ultraviolet curing nature resin composition. It is preferred that 0.005 micrometer - 1 micrometer are especially 0.01-0.1 micrometer preferably as mean particle diameter of such particle powder.

[0122]As for a rate of an ultraviolet-curing-resin constituent and particle powder, it is desirable to blend to resin composition 100 mass part, so that it may become 0.1 to 10 mass part.

[0123]Thus, a layer which stiffened formed ultraviolet curing resin may be an anti-glare layer whose Ra is about 0.1-1 micrometer, even if center line average-surface-roughness Ra is a clear hard court layer which is 1-50 nm. It can be with a surface treatment method of this invention, and plasma treatment can be carried out on these layers. Especially according to the surface treatment method of this invention, optical interference layers, such as a uniform low refractive index layer or a high refractive index layer, etc. can be provided on a substrate with surface unevenness. Since the plasma treatment of the center line average surface roughness (Ra) especially specified by JIS B 0601 can be uniformly carried out on an anti-glare layer which is 0.1-0.5 micrometer, it is desirable.

[0124]In this invention, when providing a thin film concerning this invention to a substrate side like the above-mentioned statement, it is less than \*\*5% to provide a thickness deviation to average thickness so that it may become \*\*10% desirable still more preferably, and it is preferred to provide so that it may become less than \*\*1% preferably especially.

[0125]When producing an optical film using a surface treatment method of this invention, since it is excellent in the adhesion of a coat formed to irradiate a plasma treated surface with ultraviolet rays before carrying out plasma treatment, it is preferred. It is preferred that it is 50 - 2000 mJ/cm<sup>2</sup> as UV irradiation light volume. An effect is not enough, and if 2000 mJ/cm<sup>2</sup> is exceeded, there is a possibility that modification of a substrate etc. may arise and it is not desirable at less than 50 mJ/cm<sup>2</sup>.

[0126]When producing an optical film of this invention, in order that carrying out UV irradiation after performing plasma treatment may also stabilize a formed coat at an early stage, it is effective.

[0127]For this reason, it is preferred to irradiate a plasma treated surface with 50 - 2000 mJ/cm<sup>2</sup> after plasma treatment as UV irradiation light volume. It is preferred to perform these processings after plasma treatment before a coiling process. As for a substrate after plasma treatment, it is preferred to be processed in a heating zone adjusted to 50-130 \*\* for 1 to 30 minutes.

[0128]Via direct or other layers using a surface treatment method of this invention on a base

material, An optical interference layer (low, inside, light-refractive-index layer), a stain-proofing barrier, a conductive layer, an antistatic layer, A uniform thin film which has various functions, such as an infiltrative-proof layer, can be formed, and various kinds of optical films which have these layers, i.e., an acid-resisting film, a low reflection anti-glare film, an antistatic film, a phase difference film, an optical compensation film, a light diffusing film, etc. can be provided.  
[0129]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to these.

[0130] The cellulose ester film which is a substrate was produced in accordance with the method shown in one or less example.

[0131]

(Preparation of a dope)

Methylene chloride 440 kg Ethanol 35 kg Triacetyl cellulose (the degree of acetylation: 2.65) 100kg Aerosil 200V (product made from Japanese Aerosil). 1 kg Triphenyl phosphate 8 kg. Ethylphthalyl ethyl glycolate 3 kg Tinuvin 326 (made in Tiba Specialty Chemicals) 0.4kg Tinuvin 109 (made in Tiba Specialty Chemicals) 0.9kg Tinuvin 171 (made in Tiba Specialty Chemicals) A 0.9kg solvent. It dissolved and mixed thoroughly, heating and agitating [ supplied to the well-closed container, and / supply and ] a raw material stirring. After lowering and settling to the temperature which casts a dope and performing defoaming operation, the solution was filtered using Azumi filter paper No.244 made of Azumi Filter paper, and the dope was prepared.

[0132]<<Measurement of the degree of substitution of cellulose ester>> According to the regular method, it carried out to ASTM-D 817-96.

[0133]<<Production of a cellulose ester film>> The cellulose ester film 1 was produced as follows using the dope prepared above.

[0134](Production of the cellulose ester film 1) After filtering dope liquid, it cast uniformly on a 30 \*\* stainless steel band base material at the dope temperature of 35 \*\* using the belt flow casting device. Then, after making it dry to the range which can exfoliate, the web was exfoliated from on the stainless steel band base material. The amount of residual solvents of the web at this time was 35%.

[0135] Width grasping is released after making it dry at 115 \*\*, grasping an end in a tenter after exfoliating from a stainless steel band base material, Desiccation was terminated in a 120 \*\* drying zone, carrying out roll conveyance, knurling processing 10 mm in width and 5 micrometers in height was performed to film both ends, and the cellulose ester film 1 of 80 micrometers of thickness was produced. Film width was 1300 mm and rolling-up length could be 1500 m.

[0136]<<Production of a base film>> The base film was produced as follows using the

cellulose ester film obtained above.

[0137]<Production of the base film 1> The cellulose ester film 1 produced by the above-mentioned method was used as the base film 1 as it was.

[0138]<Production of the base films 2 and 3> the following coating composition (1) to a side (field of the opposite hand of the side (b side) which was in contact with the belt base material on the occasion of flow casting film production) of the cellulose ester film 1 produced by the above-mentioned method. Extruded and carried out the coat so that it might become 13 micrometers of wet thickness, and it was made to dry with the drying temperature of 80 \*\*, and the back coat layer was painted. Let this be the base film 2. Gravure coating of the following coating composition (2) is carried out to this b side so that it may be set to 13 micrometers by wet thickness, Subsequently, after drying by the dryer part set as 80 \*\*, UV irradiation was carried out by 120 mJ/cm<sup>2</sup>, and a 4-micrometer clear hard court layer [ center-line-surface-roughness (Ra)15nm ] was provided by dry membrane thickness. Let this be the base film 3.

[0139]<Production of the base film 4> the following coating composition (1) to a side (field of the opposite hand of the side (b side) which was in contact with the belt base material on the occasion of flow casting film production) of the cellulose ester film 1 produced by the above-mentioned method. Extruded and carried out the coat so that it might become 13 micrometers of wet thickness, and it was made to dry with the drying temperature of 80 \*\*, and the back coat layer was painted. Next, gravure coating of the following coating composition (3) was carried out to b side so that it might be set to 13 micrometers by wet thickness, after drying by the dryer part subsequently to 80 \*\* set up, UV irradiation was carried out by 120 mJ/cm<sup>2</sup>, and a 5-micrometer anti-glare layer (arithmetical mean deviation of profile (Ra) 0.3 micrometer) was provided by dry membrane thickness. Let this be the base film 4.

[0140]The presentation of the coating composition (1) used for production of a base film given [ above-mentioned ] in the following and (2) and the preparing method of a coating composition (3) are shown.

[0141]

Coating composition (1) (back coat layer coating composition)

acetone 30 mass parts Ethyl acetate 45 mass parts . Isopropyl alcohol Ten mass parts  
Diacetyl cellulose 0.5 mass part Ultrafine particle silica 2% acetone dispersion liquid (Aerosil 200V: product made from Japanese Aerosil) 0.1 mass part Coating composition (2) (clear hard court layer coating composition)

dipentaerythritol hexaacrylate monomer . 60 mass parts Dipentaerythritol hexaacrylate dimer 20 mass parts Ingredient more than a dipentaerythritol hexaacrylate trimer 20 mass parts  
Dimethoxybenzophenone photoreaction initiator Four mass parts Ethyl acetate . 50 mass parts  
Methyl ethyl ketone 50 mass parts . Isopropyl alcohol SAIRISHIA 431 (mean-particle-diameter

2.5micrometer.) 50 mass parts <Preparation coating composition (3) and (for anti-glare layer production)> ethyl acetate 50 mass parts Methyl ethyl ketone 50 mass parts Isopropyl alcohol 50 mass parts (product made from Fuji SHIRISHIA Chemicals) 2.5 mass part [ ] – two or more mass parts – high-speed-stirring machine Aerosil R972V (mean particle diameter of 16 nm (product made from Japanese Aerosil)) (TK homomixer.) After it stirred by the product made from special opportunity-ized Industry and the collided type dispersion machine (product made from the Menton gaulin and Gaulin) distributed after that, the following ingredient was added and the coating composition (3) was prepared.

[0142]

dipentaerythritol hexaacrylate monomer . 60 mass parts Dipentaerythritol hexaacrylate dimer 20 mass parts Ingredient more than a dipentaerythritol hexaacrylate trimer 20 mass parts Dimethoxybenzophenone photoreaction initiator 4 mass-part profitable \*\*\*\* base films 1-4 are shown in the following table 1.

[0143]

[Table 1]

	a 面塗布層		b 面塗布層
基材フィルム1	なし	セルロースエステルフィルム1	なし
基材フィルム2	バックコート層	セルロースエステルフィルム1	なし
基材フィルム3	バックコート層	セルロースエステルフィルム1	クリアハードコート層
基材フィルム4	バックコート層	セルロースエステルフィルム1	防眩層

[0144]<<Production of a low reflection layered product>> Atmospheric pressure plasma treatment was continuously performed to the b side side of the base films 1-4 using the plasma discharge processing unit shown in drawing 2 using the base films 1-4 given in Table 1.

[0145]That is, reactant gas was changed as shown below, and four layers, a high refractive index layer (the refractive index 1.90, 22 nm of thickness), a low refractive index layer (the refractive index 1.46, 26 nm of thickness), a high refractive index layer (the refractive index 1.90, 96 nm of thickness), and a low refractive index layer (the refractive index 1.46, 87 nm of thickness), were provided in order.

[0146]To the product jacket roll base material made from stainless steel (not shown [ the cooling function ] to drawing 2) which has a cooling function by cooling water as the rotating electrode 25 here. The rotating electrode which covers alumina with ceramic flame spraying 1 mm, stiffens the solution which diluted the tetramethoxy silane with ethyl acetate after that after spreading desiccation and by UV irradiation, performs sealing, and has a dielectric was manufactured and grounded (grounding). On the other hand, as the counterelectrode 24, to the stainless steel rod in the air, the same dielectric as the above was covered with the conditions, and was made into the electrode group which counters. The inter-electrode spare time of the rotating electrode 25 and the counterelectrode 24 which counters was 1 mm. The



use power supply used for discharge plasma generating is 13.56 MHz in frequency in JEOL Co., Ltd. make RF generator JRF-10000. Discharge density performed plasma discharge processing as  $300 \text{ W-min/m}^2$ . However, the rotating electrode was rotated using the drive. [0147]The presentation of the mixed gas (reactant gas) used for plasma treatment is described below.

(For low refractive index layer formation)

Inactive gas: Argon 98.2% reactant gas : Hydrogen gas 1.5% reactant gas : Tetramethoxy silane 0.3% (for high refractive index layer formation)

Inactive gas: Argon 98.7% reactant gas 1: Hydrogen gas 1% reactant gas : Tetraisopropoxy titanium About the low reflection layered product obtained 0.3%, as a result of performing visual evaluation, nonuniformity was not accepted but the evaluation result of O was obtained. When evaluated by measuring reflectance as follows, low reflectance was obtained in [ wavelength ] 450-650 nm. Although ten points were measured at the approximately equivalent interval to the width direction, any measurement result was low reflectance in the wavelength range of 450-650 nm. The reflection-spectrum measurement result of the optical film 3 obtained by drawing 13 was shown. The result also with the same optical films 1, 2, and 4 was obtained.

[0148]<<Measurement of reflectance>> The spectral reflectance of the low reflection layered product measured reflectance on condition of regular reflection 5 times using the spectrophotometer U-4000 type (made by Hitachi). After measurement carried out the surface roughening process of the rear face by the side of observation, it performed optical absorption processing using the black spray, prevented reflection of the light on the rear face of a film, and measured reflectance (wavelength of 400-700 nm).

[0149]<<Visual evaluation>> Optical absorption processing is performed for a width hand overall-width x500cm sample at the rear face using a black spray, reflection of a fluorescent lamp is observed from the surface, and the nonuniformity of catoptric light is evaluated.

[0150]

O nonuniformity is not known -- O -- plasma treatment was performed using the device of drawing 2 using the comparative example 1 base film 3 which \*\* nonuniformity to which nonuniformity is accepted slightly worries. However, a deed and supply from other gas inlets were not performed only from the gas inlet 30 where supply of reactant gas was provided in the method of the forefront of the electrodischarge treatment part. Nonuniformity was accepted and the optical film of comparison obtained as a result was \*\* on the standard of visual evaluation.

[0151]There was much sludge to the counterelectrode near the gas inlet, and processing continuously stable for a long time was not able to be performed.



[0152]The thin film in which a refractive index decreases from the substrate side was formed in b side of the example 2 base film 3. The plasma discharge processing unit shown by drawing 1 was used. To the product jacket roll base material made from stainless steel (not shown [ the cooling function ] to drawing 1) which has a cooling function by cooling water as the rotating electrode 25 here. The rotating electrode which covers alumina with ceramic flame spraying 1 mm, stiffens the solution which diluted the tetramethoxy silane with ethyl acetate after that after spreading desiccation and by UV irradiation, performs sealing, and has a dielectric was manufactured and grounded (grounding). On the other hand, what covered the same dielectric as the above with the conditions, and produced it was made into the counterelectrode group 24 which counters to the stainless steel rod.

[0153]The inter electrode distance of the rotating electrode 25 and the counterelectrode 24 was 1 mm. The use power supplies used for discharge plasma generating are the JEOL Co., Ltd. make and RF generator JRF-10000, and frequency is 13.56 MHz. Discharge density performed plasma discharge processing as  $300 \text{ W-min/m}^2$ . However, the rotating electrode was rotated using the drive.

[0154]The mixed gas used for plasma treatment changes the mixture ratio of two kinds of following gas (the gas L and gas H) as follows, It was made to change from the substrate conveyance upstream gas inlet 30a (reactant gas is supplied to the discharge section by the side of the Mogami style) to the substrate conveyance downstream side gas inlet 30k (reactant gas is supplied to the discharge section by the side of the lowest style), and supplied. As a result, in the refractive index of a portion with the obtained thin film near a substrate, the surface had a refractive index of 1.46 by 2.0.

[0155]

[Table 2]

	各ガス導入口から各放電部に供給するガスの混合比										
	30a	30b	30c	30d	30e	30f	30g	30h	30i	30j	30k
ガスL	0	1	2	3	4	5	6	7	8	9	10
ガスH	10	9	8	7	6	5	4	3	2	1	0

[0156]As a result of performing visual evaluation, nonuniformity was not accepted but evaluation of O was obtained. The portion with the membranous ingredient near a substrate has main titanium oxide, the oxidized silicon ingredient increased gradually, and the surface had the presentation inclination of mainly consisting of oxidized silicon. According to this invention, it was checked that the thin film which has such the characteristic can be obtained easily.

[0157]The reactant gas used for plasma treatment is described below.

< -- low-refractive-index side reactant gas; -- gas L> inactive gas: -- argon . 98.7% reactant

gas: -- hydrogen gas 1% reactant gas: -- tetramethoxy silane 0.3% -- <high refractive index layer side reactant gas; -- gas H> inactive gas: -- argon 98.7% reactant gas: -- hydrogen gas 1% reactant gas: -- tetraisopropoxy titanium . In accordance with the method described below, it evaluated by producing a polarizing plate using the optical films 1-4 produced in example 3 Example 1 0.3%.

[0158]In accordance with the following method, the polarizing plate 1 using the optical film 1 as a protective film for polarizing plates was produced.

[0159](Production of a polarization film) Uniaxial stretching (one 5 times the draw magnification [ temperature of 110 \*\*, ] of this) of the 120-micrometer-thick polyvinyl alcohol film was carried out. This was immersed in the solution which consists of the iodine 0.075g, 5 g of potassium iodide, and the water 100g for 60 seconds, and it was immersed in the 68 \*\* solution which subsequently consists of the potassium iodide 5g, the boric acid 7.5g, and the water 100g. This was rinsed, it dried and the polarization film was obtained.

[0160](Production of a polarizing plate) It ranked second, the polarization film and the protective film for polarizing plates were pasted together according to the following steps 1-5, and the polarizing plate was produced.

[0161]Process 1: It cuts off one sheet each in with the longitudinal direction of 30 cm, and a width direction of 18 cm size, and is immersed in the sodium hydroxide solution of 2 mol / L for 90 seconds at 45 \*\*, and subsequently, it rinsed and the optical film 1 and the cellulose ester film 1 which were produced in Example 1 were dried. The protective film of detachability was stuck on the low refractive index layer side, and the surface was protected from alkali.

[0162]Process 2: Said polarization film cut out in with the longitudinal direction of 30 cm and a width direction of 18 cm size was immersed for 1 to 2 seconds into the polyvinyl alcohol adhesives tub of 2 mass % by solid content %.

[0163]Process 3: The superfluous adhesives which adhered to the polarization film at the process 2 were removed lightly, and it laminated on the optical film 1 which processed it at the process 1, and also it laminated and the same optical film 1 has been arranged so that adhesives may be touched.

[0164]Process 4: Superfluous adhesives and air bubbles were removed and pasted together with the hand roller from the end of the laminated material of the polarization film and the protective film sample 1 which were laminated at the process 3. The pressure of the hand roller was made into 30-40-N[cm]<sup>2</sup>, and roller speed was made into 2 m/min.

[0165]The drying process of the sample produced at the process 4 in the dryer of 5:80 \*\* of processes was carried out for 3 minutes, and the polarizing plate 1 of this invention was produced.

[0166]The polarizing plates 2-4 were similarly produced, respectively except having used the

optical films 2-4, respectively. The comparative polarizing plate was produced using the optical film of the comparative example 1.

[0167]The polarizing plate of the outermost surface of a commercial liquid crystal display panel (NEC make and color liquid crystal display MultiSync LCD1525J model name LA-1529HM) was exfoliated carefully, and the polarizing plates 1-4 of this invention or the comparative polarizing plate 1 which united the polarization direction here was stuck. Each liquid crystal display panel does not have the nonuniformity of catoptric light to the liquid crystal display panel which used the polarizing plate of the comparative example, and excelling in display performance was checked. On the other hand, as for the liquid crystal display panel using the comparative polarizing plate 1, nonuniformity was observed in catoptric light.

[0168]

[Effect of the Invention]The optical film which could form the uniform thin film on the surface of the base film, and was excellent in the optical property by the surface treatment method using the plasma discharge of this invention is obtained.

[Translation done.]